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BINDER MODEL SYSTEM TO BE USED FOR DETERMINATION OF PREPOLYMER FUNCTIONALITY

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I OBJECTIVE

The objective of this work has been to develop a method for determining the functionality distribution of prepolymers used for rocket binders. Work performed during early stages was concerned with accurately determining the gel point of a model polyester system containing a single trifunctional crosslinker. Subsequent work involved applying these methods to more complicated model systems containing a second trifunctional crosslinker, monofunctional ingredients, or a higher functionality crosslinker. Correlations of observed with theoretical gel points for these systems would allow the methods to be applied directly to prepolymers.

II INTRODUCTION AND SUMMARY

The current method of prepolymer functionality distribution determination is a combination of reactive group assay and molecular weight measurement. Work performed at the Jet Propulsion Laboratory[1] has shown that the basis for a method of determining the functionality distribution of prepolymers can be developed by extending Flory's network theory.[2]

The theory defines gelation criteria for systems containing a single trifunctional unit (crosslinker). It requires that the polymerizations proceed without side reactions and that like reactive groups behave the same regardless of the size of the chain to which they are attached. Moreover, our application of the theory requires the reactions proceed to completion and at a reasonable rate. To test this theory, polyesterifications (catalyzed by p-toluenesulfonic acid) were carried out where the reaction mixture was vigorously stirred and heated in contact with dry N_2 sweep. The gel point could be very accurately determined by monitoring the viscosity of the reaction mixture. Experimental details are contained in our Final Report for 1968-1970.[3]

Flory's theory has been extended to account for systems where the functional groups on the crosslinker are of different reactivity, and to systems containing two different trifunctional crosslinkers. A second theory due to Stockmayer[4,5] can be applied directly only to these latter systems; the predicted gel points, however, differ considerably from those predicted by our extension of Flory's theory. Stockmayer's theory cannot be directly applied to the former systems since the unequal reactivity of the functional groups on the crosslinker cannot be accounted for. A complete treatment of the theory is contained in the first Final Report.[3]

The results of work performed during the first two years of this project are summarized below.

1. Flory's theory was verified for simple (2/3,2)* systems, i.e., systems containing a triacid, a diacid, and a diol under excess alcohol conditions. It was found that at the gel point the equation

$$r = \rho + 1 \tag{1}$$

was obeyed, where r is the ratio of alcohol to acid groups and ρ is the mole fraction of acid groups contributed by the triacid.†

2. For the same systems under excess acid conditions, i.e., (3,2/2) systems, Eq. (1) was again obeyed except in the case where the groups on the triacid were of different reactivity. In this case, the crosslinker had one secondary and two primary carboxyl groups and tended to behave as a difunctional unit since long chains rather than crosslinks are favored at equilibrium. This phenomenon is not observed with excess hydroxls since all the carboxyl groups are forced to react, i.e., the reactions proceed to completion.

If x is the reactivity ratio of the secondary to primary groups then, at the gel point, the data obey the equation

$$R = \frac{2 + x + 3\rho x}{(2+x)(1-\rho/3+\rho x/3)} \tag{2}$$

where R is the ratio of acid to hydroxyl groups. (Note that (2) reduces to (1) when x = 1.0).

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* This notation will be used throughout the report to denote the systems under consideration. The numbers refer to the functionalities of the monomers, those to the left of the diagonal refer to the type of group in excess.

† The symbols ρ_A and ρ_B will be used to denote acid and hydroxyl contributions, respectively. In general, R will refer to excess carboxyl systems and r to excess hydroxyl systems.

Gel points obtained for these systems differed from other systems in that the mixtures did not gel at a discrete point, but increased slowly to beyond the limits of detection of the instrument. Consequently, the gel point was obtained by extrapolating the viscosity versus composition data to the point where the viscosity just becomes infinite. The method of extrapolation and its mathematical justification are given in the Appendix.

3. Flory's theory was extended[6] to account for monofunctional components. The systems (2/3,2,1) and (2,1/3,2) with excess hydroxyls were investigated and found to conform to the theory fairly well.

4. Flory's theory was again extended[6], this time to account for (3,2/3,2) systems under excess hydroxyl conditions. Gel points predicted by Flory's theory and by Stockmayer's theory were compared with experimental results; the data agreed well with the former and systematically disagreed with the latter.

Work for the current year has been primarily concerned with correlating theoretical and experimental gel points for more complicated systems that more closely approximate actual prepolymers. Several parameters are available from the theory which may be used for the correlation. The most important of these is the probability α that any given one of the functional groups of a crosslinker leads, via a sequence of bifunctional units, to another branch rather than to a terminal group. Flory has shown that

$$\alpha_c = \frac{1}{f-1} \tag{3}$$

where α_c is the critical value of α at which gelation begins and f is the functionality of the crosslinker. Thus, for a trifunctional crosslinker, $\alpha_c = 1/2$.

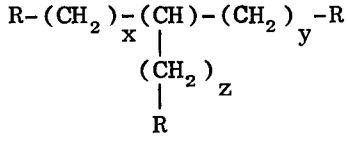
Most of the gel point determinations have been made for model systems where α's are readily calculable in terms of the composition parameters R, r, ρ, and σ according to Flory's theory (see Final Report, 1968-1970, Section III-B). The quantity R (or r) is used in cases where a comparison with another theory is to be made, or when the parameters ρ or σ are unknown, as in the case of prepolymers.

Gel point determinations for systems containing commercial prepolymers have also been made. Emery Dimer and Trimer acid, several of Humko's Hysterene products, and Telegen-S have been investigated.

III RESULTS AND DISCUSSION

A. Analysis of Crosslinkers

The choice of crosslinkers to be used in polyesterifications became an important factor in the early stages of this work. The optimum crosslinker may be represented by structure I

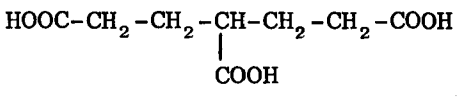


I

when x, y, and z are all greater than three, and R is either a hydroxyl or carboxyl group. Such a structure should have equally reactive functional groups, a low melting point, and a reasonably low vapor pressure. There should be no steric hindrance even after two of the R groups have reacted. The tendency for ring formation should be quite low (minimum 10-member ring), and the aliphatic structure is inherently nonreactive.

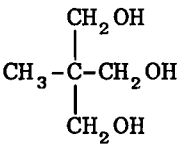
In lieu of this idealized compound, actual crosslinkers were either obtained from commercial sources or synthesized. Carbon-hydrogen analyses, along with acid and hydroxl numbers, were used as criteria for purity, which was greater than 99% in all cases. Each crosslinker is discussed in turn.

1. 1,3,5-Pentanetricarboxylic Acid (PTA)



This compound was obtained commercially and used extensively during the first two years. When it was employed in systems with excess alcohol groups, gel points agreed well with theory, i.e., conformed to Eq. (1). However, the carboxyl group attached to the secondary carbon atom is less reactive than the other two; consequently, data obtained for systems with excess carboxyl groups obeyed Eq. (2) with x = 0.20. Details of the investigation of this compound are contained in the first Final Report.[3] It has been used subsequently for all general systems involving excess hydroxyl conditions (see sections B, C, and D).

2. 1,1,1-Trimethylol Ethane (TME)



The results from four different experiments using this compound with decanediol and sebacic acid under excess hydroxyl conditions ((3,2/2) systems) agreed quite well with theory (see Table 1, Runs 14-17). Consequently, TME was used for all general runs requiring a trihydroxy crosslinker under conditions of excess hydroxyls.

The results obtained for the (2/3,2) excess carboxyl systems, however, consistently deviated from theory (Table 1). The reason for the average value of $\alpha = 0.557$ is not yet known; however, the discrepancy is probably due to steric hindrance after two of the hydroxyls have reacted. Under these conditions, all of the hydroxyls are forced to react, while under excess hydroxyl conditions they obviously are not. Thus, as with PTA, this compound is unsuitable as a crosslinker when its own groups are not in excess.

3. 1,3,5-Benzenetriacetic Acid (BTA)

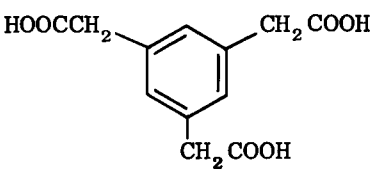


Table 1

GEL POINTS FOR SYSTEMS CONTAINING TME

Run	ρ_B	α	±*	Excess
1	.108	.587	.015	COOH
2	.202	.559	.017	COOH
3	.293	.552	.012	COOH
4	.371	.552	.008	COOH
5	.450	.557	.008	COOH
6†	.450	.556	.008	COOH
7	.532	.560	.014	COOH
8	.547	.557	.013	COOH
9	.615	.551	.011	COOH
10	.703	.553	.010	COOH
11	.830	.555	.009	COOH
12	.915	.552	.010	COOH
13	1.00	.548	.015	COOH
14	.25	.501	.001	OH
15	.50	.503	.001	OH
16	.75	.502	.001	OH
17	1.00	.50	.01	OH

* Tolerance

† No solvent.

This compound was prepared by the method of Newman and Lowrie.[6] The results of gel point determinations made on systems containing BTA, decanediol, and sebacic acid are shown in Table 2.

α-Values preceded by the symbol < indicate systems that gelled at the first composition tested and therefore represent only an upper limit for α.

Runs 1-3 established this crosslinker as a suitable replacement for PTA under excess acid conditions. Since the carboxyl groups on the BTA molecule should be equally reactive, these data lend support to the assertion that the carboxyl groups on PTA do not have equal reactivity.

Anomalous behavior was observed for BTA under excess hydroxyl conditions, when all of the α values were below 1/2 signifying early gelation. However, extraction of the resulting products with benzene yielded no gel in any of the runs. What could be occurring is the formation of very large inflexible molecules of high viscosity. A high solvent (Nujol) concentration, as much as 67% in Run 5, did not affect the result, but the greatest discrepancy (Run 7) was observed when the system contained no solvent. This pseudogelation phenomenon makes BTA unsuitable as a crosslinker under excess hydroxyl conditions.

4. 1,3,5-Trimethylolbenzene (BTM)

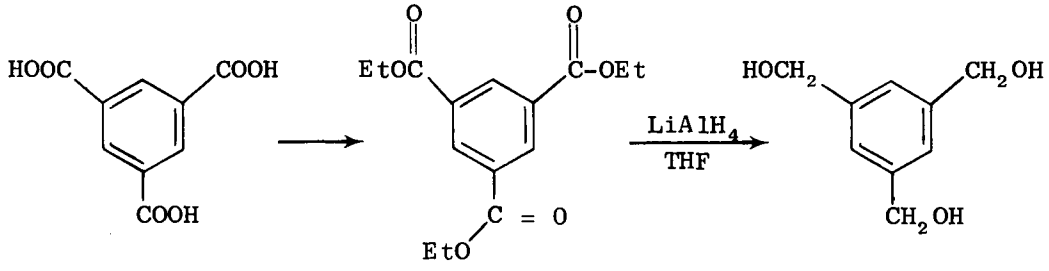


Table 2

GEL POINTS FOR SYSTEMS CONTAINING BTA

Run	ρ_A	α	±	Excess
1	.15	.511	.006	COOH
2	.30	.511	.004	COOH
3	.45	.506	.002	COOH
4*†	.198	.486	.010	OH
5*†	.200	<.488	--	OH
6*	.201	<.478	--	OH
7*	.242	.425	.005	OH
8*	.250	<.490	--	OH
9*†	.495	.486	.005	OH

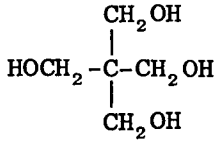
* Extracted--no gel found.
† Contained solvent.

This hydroxy analog of BTA was synthesized from trimesic acid according to the above reaction scheme. Results of gel point determinations made using this compound as crosslinker with sebacic acid and decanediol are shown in Table 3.

Under excess acid conditions, BTM behaved the same as TME, i.e., it gelled consistently late. This would seem to indicate that the problem is not chemical in nature since the two structures are very different.

Under excess hydroxyl conditions, BTM systems exhibited the same pseudogelation observed in BTA systems (Runs 1 and 2). This is not surprising since these compounds are structurally similar. However, in contrast to BTA, extraction of the products from Runs 3 and 4 revealed almost 40% insolubles. This phenomenon may again be explained in terms of the structure. The same structures responsible for the rapid increase in viscosity near the gel point could be linked up at these higher ρ values to form local gel sites which would be insoluble in benzene. This hypothesis, however, contradicts the results of a statistical theory of molecular size distributions put forth by Flory.[7] In any case, BTM appears to be unsuitable for use as a model crosslinker under either excess hydroxyl or excess acid conditions.

5. Pentaerythritol (PTL)



The results of gel point determinations for systems employing sebacic acid decanediol and PTL as crosslinker are shown in Table 4. The theoretical α_c for a tetrafunctional crosslinker is 1/3, as calculated by Eq. (3); the common gel point and interval for runs 8-10,

Table 3

GEL POINTS FOR SYSTEMS CONTAINING BTM

Run	ρ_B	α	$\pm$	Excess
1*	.30	.501	.009	OH
2*	.50	<.476	--	OH
3	.70	<.490	--	OH
4	.70	<.467	--	OH
5	.163	.536	.008	COOH
6	.189	.586	.020	COOH
7	.277	.582	.014	COOH
8	.588	.576	.010	COOH

* Extracted--no gel found.

Table 4

GEL POINTS FOR SYSTEMS CONTAINING PTL

Run	ρ_B	α	$\pm$	Excess
1	.30	.417	.015	OH
2	.40	.424	.006	OH
3	.50	.347	.004	OH
4	.60	.352	.005	OH
5	.70	<.326	--	OH
6	.80	<.314	--	OH
7	1.0	<.318	--	OH
8	.50	.414	.025	COOH
9	.50	.431	.028	COOH
10*	.50	.428	.031	COOH

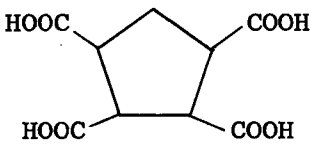
* No solvent.

i.e., excess acid conditions are $\alpha_c = 0.421 \pm 0.018$ or a deviation of 33% from the theoretical α_c. PTL, which is structurally quite similar to TME, thus also gels consistently late under conditions of excess acid possibly because steric hindrance prevents complete reaction of the polyfunctional alcohol.

Under excess hydroxyl conditions, there seems to be a trend toward decreasing α with increasing ρ_B. A side reaction where two PTL molecules react to form an ether containing six hydroxyl groups might account for this trend. The effects of increased functionality of individual units and of a decrease in the excess hydroxyl groups would be especially noticeable at high ρ values.

Under either excess acid or alcohol conditions, PTL appears to be unsuitable for use as a tetrafunctional crosslinker.

6. 1,2,3,4-Cyclopentanetetracarboxylic Acid (CPT)



Only two experiments were performed using this compound as crosslinker, a (4,2/2) and a (2/4,2) system. Both employed decanediol and sebacic acid as the difunctional components. The first was carried out under excess hydroxyl conditions yielding $\alpha = 0.379 \pm 0.012$ at $\rho = 0.406$. This is near enough to the theoretical gel point (+13.8% discrepancy) to warrant more determinations at different ρ values to see if CPT behaves like PTL under excess hydroxl conditions, i.e., shows a trend of decreasing α with increasing ρ. If this is the case, the theoretical calculation of the α's should be reinvestigated; α's reported in Table 4 are computed according to Eq. (17) of the first Final Report, where we have assumed the equation holds for systems where a tetrafunctional branch unit has replaced every trifunctional branch unit. Values of r at gelation also differ from the theoretical values predicted

by Stockmayer's theory for both CPT and PTL. This is to be expected, however, since Flory and Stockmayer predict the same gel points for systems containing only one crosslinker (see Part B below).

The second experiment, under excess acid conditions, yielded no gel for α values up to 0.55 with $\rho = 0.5$. The run was discontinued after this point because of the dark color of the reaction mixture.

7. Other Crosslinkers

Several other compounds were found to be unsuitable as crosslinkers for various reasons. Glycerol, tricarballylic acid, and 1,2,6-hexanetriol decomposed under the experimental conditions used; 1,3,5-benzenetricarboxylic acid and nitrilotriacetic acid were too high melting; and trimethylolpropane sublimed out of the reaction mixture.

8. Effect of Catalyst

In an effort to determine the reason for the observed late gelation in some of the systems, the effect of catalyst (p-toluenesulfonic acid) concentration was investigated. If under certain circumstances the catalyst permanently reacts with the crosslinker, the effective ρ-value would be reduced which would account for late gelation. The effect would be expected to be accentuated at higher catalyst levels.

Accordingly, gel determinations were made for (2/3,2) systems containing TME over a 50-fold range in catalyst concentration. The results in Table 5 show that only at very large catalyst levels is there any real change in α. The effect is not sufficient to explain the large consistent discrepancy at low catalyst levels. An experiment with $\rho_B = 0.5$ was repeated using the methyl ester of the catalyst (0.5%) with no change in gel point. Thus catalyst interaction does not appear to be responsible for the observed discrepancy in α.

Table 5

EFFECT OF ρ-TOLUENESULFONIC ACID CATALYST ON α-VALUES FOR (2/3,2) SYSTEMS CONTAINING TME

ρ_B	Cat. (%)	α	±
0.45	0.2	0.555	0.015
0.45	0.5	0.557	0.008*
0.44	5.0	0.579	0.008
0.43	10.0	0.583	0.013

* Normal level.

9. Conclusions

The behavior of the various crosslinkers is summarized in Table 6.

Table 6

SUMMARY OF CROSSLINKERS

Excess Group	Acids			Alcohols		
	PTA	BTA	CPT	TME	BTM	PTL
OH	OK	Early	--	OK	Early	Varied
COOH	Late	OK	Late	Late	Late	Late

For applicability of the theory, the esterification reactions must proceed with no side reactions. We have assumed this to be the case for those systems that conform to the theory. However, under the experimental conditions (acid catalyst and 140°C) it is possible for side reactions to occur in certain systems. Side reactions involving one of the groups on the trifunctional compound would produce a difunctional component which would account for the observed late gelation.

Thus we are left with only three combinations of crosslinker and excess group that agree with theory (see Table 6). All subsequent experiments have been carried out using these combinations.

With reference to the objective of this research, the inability of all crosslinkers to conform to theory presents another problem. Suppose, for example, that a hydroxy-terminated prepolymer under investigation contains a trifunctional component that behaves like the BTM molecule. Gel points for these systems would be meaningless; moreover, an independent method would have to be developed to check whether or not the system is conforming to theory.

Consequently, we feel that any future research in this area should place initial emphasis on further understanding the molecular behavior of systems undergoing gelation. The synthesis of an optimum crosslinker (Structure I) would be invaluable in this regard. Also, there are theories of molecular size distribution for these systems[7,8] that may assist in studying their behavior.

B. (3,2/3,2) Systems

Flory's theory has been generalized to account for systems containing two different trifunctional crosslinkers, a diol and a diacid, i.e., (3,2/3,2) systems. Preliminary results were obtained for these systems and are contained, along with details of the theoretical extension, in the first Final Report.[3] In general, we found that Flory's approach rather than that of Stockmayer more accurately described the data.

Recently, Stockmayer suggested[9] that theoretical gel points for (3,2/3,2) systems should be considerably different from those given in our published results.[10] He extends Flory's model to include two different trifunctional ingredients and arrives at the same gelation criteria as predicted by his own theory.[4,5] In particular, for the (3/3) case he finds $r_c = 4$ (the ratio of alcohol to acid groups at gelation) instead of 3, as predicted by our extension of the Flory model.[10]

Experimental r_c's for each of these systems can be determined without appealing to either theory and as such can serve as an independent measure. Thus, several additional (3,2/3,2) systems have been investigated using decanediol and sebacic acid, with pentanetricarboxylic acid and trimethylolethane as crosslinkers under excess hydroxyl conditions.

The cumulative results are shown in Table 7; column headings are defined as follows:

ρ_A, ρ_B: mole fraction of acid and alcohol groups, respectively, contributed by the trifunctional molecules

α: branching coefficient calculated from the extended Flory model

$\Delta\alpha$: percent deviation in the experimental α from the theoretical 0.5

r_e: experimental r value, $r_e = \Sigma OH/\Sigma COOH$

r_f, r_s: r values predicted by the extended Flory and Stockmayer models, respectively

$\Delta r_f, \Delta r_s$: percent deviations of r_f and r_s from r_e.

The data clearly show a close correlation with our extension of the Flory model and a systematic disagreement with the Stockmayer model. Since the percent deviations in α tended to increase with decreasing ρ, the difunctional starting materials (sebacic acid and decanediol) were repurified by recrystallization, the former from acetone and the latter from 50% aqueous ethanol. The purity of all the starting ingredients was rechecked by carbon-hydrogen analysis and found to be adequate ($\pm 0.2\%$). Runs 8 and 15 were conducted with these repurified monomers with virtually no change in the results.

Both of the theories require the absence of side reactions, especially ring formation. The fact that our data coincide with gel points predicted by both theories (to within a reasonable experimental error) for systems containing PTA or TME under excess hydroxyl conditions ((2/3,2) systems) suggests that ring formation is indeed eliminated at equilibrium in these systems. If, for some reason, ring formation begins to occur in, say, the (3/3) systems due to the absence of difunctional components, the crosslinker concentration would be effectively

Table 7

GEL POINTS FOR (3,2/3,2) SYSTEMS CONTAINING PTA AND TME

Run	ρ_A	ρ_B	α	$\Delta\alpha$	r_e	r_f	Δr_f	r_s	Δr_s
1*	.005	0.50	.502	0.4	1.503	1.506	0.20	1.508	0.33
2*	.505	0.10	.501	0.2	1.652	1.653	0.06	1.656	0.24
3	.097	0.10	.523	4.6	1.187	1.206	1.65	1.207	1.65
4*	.113	0.50	.503	0.6	1.626	1.633	0.43	1.670	2.71
5*	.210	0.50	.495	1.0	1.767	1.750	0.96	1.815	2.72
6	.240	0.25	.514	2.8	1.504	1.532	1.86	1.550	3.06
7*	.512	0.30	.503	0.6	1.904	1.918	0.74	1.966	3.26
8†	.285	0.30	.514	2.8	1.604	1.640	2.24	1.671	4.18
9	.371	0.40	.509	1.8	1.819	1.850	1.70	1.919	5.50
10*	.328	0.50	.506	1.2	1.873	1.894	1.12	1.992	6.36
11	.368	0.40	.515	3.0	1.793	1.846	2.95	1.915	6.80
12	.461	0.50	.506	1.2	2.031	2.058	1.33	2.192	7.92
13*	.526	0.50	.511	2.2	2.085	2.138	2.54	2.289	9.79
14	.464	0.50	.515	3.0	1.997	2.062	3.25	2.196	9.96
15†	.667	0.70	.501	0.2	2.469	2.474	0.20	2.834	14.8
16	.651	0.70	.505	1.0	2.429	2.455	1.07	2.807	15.6
17	.730	0.75	.500	0.0	2.581	2.582	0.04	3.028	17.1
18	.870	0.90	.502	0.4	2.819	2.824	0.18	3.553	26.0
19	1.00	1.00	.501	0.2	2.997	3.000	0.10	4.000	33.3
20	1.00	1.00	.500	0.0	3.000	3.000	0.00	4.000	33.3
21*	1.00	1.00	.500	0.0	3.001	3.000	0.03	4.000	33.3

* No solvent.
† Repurified monomers.

reduced causing the system to gel later. Furthermore, any other side reactions involving the functional groups on the crosslinkers would produce the same effect.

Thus there seems to be no way to account for the gelation of (3/3) systems at $r_c = 3.0$, if indeed Stockmayer's equation is correct.

C. General Systems

Having established Flory's extended theory as a useable model for (3,2/3,2) systems, we then applied it to more general (3,2/3,2,1) and (3,2,1/3,2) systems. This can be done without any further modification using Eq. (17) of the first Final Report.[3] If we assume that $\alpha = 1/2$ for these general systems, Eq. (17) can be rearranged to give

$$\rho_B r^2 + (\rho_A - 2\sigma_A\rho_B^2 - 4\rho_A\rho_B - \rho_B\sigma_A\sigma_B)r - (\rho_A\sigma_A\sigma_B + 2\sigma_B\rho_A^2) = 0$$

Solving this equation by means of the quadratic formula yields r_c.

The effect of monofunctional ingredients on the gel point has been theoretically investigated by other workers and the resulting equations, which are essentially modifications of Stockmayer's equation, were collected in a recent publication.[11] These, along with Stockmayer's equation, are shown below for our systems (i.e., up to trifunctional ingredients):

$$r_s = (2\rho_A + \sigma_A)(2\rho_B + \sigma_B)$$

$$r_1 = (2\rho_A + \sigma_A)(2\rho_B + \sigma_B)(1 - \mu_A - \mu_B - \mu_A\mu_B)$$

$$r_2 = [\sigma_A + 2\rho_A(1-\mu_A)]\,[\sigma_B + 2\rho_B(1-\mu_B)]$$

The symbols ρ_A, σ_A, μ_A refer, respectively, to the mole fraction of tri-, di-, and monofunctional ingredients of one type (acid or alcohol), and ρ_B, σ_B, μ_B refer to the other. Each r is the ratio of alcohol to acid groups at gelation.

The results of gel point determination for systems containing monofunctional ingredients are contained in Table 8. All were conducted under excess hydroxyl conditions using TME and/or PTA as cross-linkers, except Runs 7 and 18, which employed BTA and TME under excess acid conditions. The monofunctional ingredients are stearic acid and octadecanol. Column headings are the same as in Table 7 with the obvious addition of r_1 and r_2, and their corresponding percent deviations Δr_1 and Δr_2. The headings f_a and f_b are the functionalities of the carboxyl and hydroxyl model prepolymers, respectively (e.g., 2.0 indicates a completely bifunctional model prepolymer).

Of the 44 runs listed in Table 8, only 39 actually gelled. Critical r's from each of these were compared with the theoretical r's described above to determine which of the equations best describes these systems. The results, shown below, are inconclusive. Note that the systems behave similarly regardless of the type of monofunctional ingredient (acid or alcohol) and consequently are grouped in pairs.

Type of System	No. of Runs	Closest Value
(2/3,2,1) (2,1/3,2)	20	r_f and r_s
(3,2/2,1) (3,2,1/2)	4	r_1
(3,1/3) (3/3,1)	2	r_f
(3,2,1/3,2) (3,2/3,2,1)	13	distributed between r_1, r_2 and r_f

Table VIII

GEL POINTS FOR GENERAL SYSTEMS

Run	ρ_A	σ_A	ρ_B	σ_B	f_A	f_B	α	$\Delta\alpha$	r_e	r_f	Δr_f	r_s	Δr_s	r_1	Δr_1	r_2	Δr_2
1	.505	.495	0.0	.950	2.0	1.905	.498	0.4	1.434	1.430	-0.28	1.430	-0.28	1.358	-5.30	1.430	-0.28
2	.255	.745	0.0	.948	2.0	1.901	.498	0.4	1.192	1.190	-0.17	1.190	-0.17	1.128	-5.37	1.190	-0.17
3	.752	.248	0.0	.950	2.0	1.905	.504	0.8	1.654	1.664	0.60	1.664	0.60	1.581	-4.41	1.664	0.60
4	~.1	~.9	~.05	~.9	2.0	1.90	>.513	--	--	--	--	--	--	--	--	--	--
5	.478	.522	.050	.900	2.0	1.90	.516	3.2	1.444	1.478	2.35	1.478	2.35	1.404	-2.77	1.471	1.87
6	.098	.902	.050	.900	2.0	1.90	.525	5.0	1.083	1.098	1.39	1.098	1.39	1.043	-3.69	1.093	0.92
7	.200	.800	.445	.533	2.0	1.924	.541	8.2	1.574	1.662	5.59	1.708	8.51	1.670	6.10	1.684	6.99
8	0.0	1.0	.500	.475	2.0	1.905	.532	6.4	1.415	1.475	4.24	1.475	4.24	1.438	1.63	1.450	2.47
9	.505	.470	0.0	1.0	1.905	2.0	.498	0.4	1.484	1.480	-0.27	1.480	-0.27	1.443	-2.76	1.455	-1.95
10	.254	.708	0.0	1.0	1.902	2.0	.502	0.4	1.214	1.216	0.16	1.216	0.16	1.170	-3.62	1.197	-1.40
11	.751	.236	0.0	1.0	1.905	2.0	.501	0.2	1.735	1.738	0.17	1.738	0.17	1.715	-1.15	1.718	-0.98
12	.106	.844	0.50	0.50	1.895	2.0	.494	1.2	1.564	1.550	-0.90	1.584	1.28	1.505	-3.77	1.568	0.26
13	.696	.292	.750	.250	1.926	2.0	.515	3.0	2.433	2.522	3.66	2.947	21.1	2.912	19.7	2.918	19.9
14	.455	.522	.50	.50	1.920	2.0	.525	5.0	1.911	2.016	5.49	2.148	12.4	2.099	9.84	2.117	10.78
15	.096	.860	.50	.50	1.907	2.0	.515	3.0	1.512	1.547	2.31	1.578	4.37	1.509	-0.20	1.565	3.51
16	.189	.763	.50	.50	1.888	2.0	.523	4.6	1.590	1.653	3.96	1.712	7.67	1.629	2.45	1.684	5.91
17	.474	.503	.10	.90	1.916	2.0	.519	3.8	1.545	1.594	3.17	1.596	3.30	1.559	0.91	1.572	1.75
18	.458	.519	.10	.90	1.919	2.0	.535	7.0	1.492	1.576	5.63	1.579	5.83	1.542	3.35	1.555	4.22
19	.441	.537	.20	.80	1.924	2.0	.545	9.0	1.560	1.687	8.14	1.703	9.17	1.665	6.73	1.680	7.69
20	0.0	.953	.50	.50	1.910	2.0	.520	4.0	1.394	1.430	2.58	1.430	2.58	1.362	-2.30	1.430	2.58
21	.504	.496	0.0	.890	2.0	1.802	.499	0.2	1.340	1.339	-0.07	1.339	-0.07	1.191	-11.1	1.339	-0.07
22	.255	.745	0.0	.890	2.0	1.802	.505	1.0	1.112	1.117	0.45	1.117	0.45	0.994	-10.6	1.117	0.45
23	.753	.247	0.0	.890	2.0	1.802	.503	0.6	1.551	1.560	0.58	1.560	0.58	1.389	-10.4	1.560	0.58
24	0.0	1.0	.250	.667	2.0	1.801	.580	16.0	1.098	1.167	6.28	1.167	6.28	1.070	-2.55	1.126	2.55
25	.243	.757	0.0	.889	2.0	1.801	.521	4.2	1.088	1.105	1.56	1.105	1.56	.982	-9.74	1.105	1.56
26	.504	.442	0.0	1.0	1.802	2.0	.500	0.0	1.450	1.450	0.00	1.450	0.00	1.372	-5.37	1.376	-3.72
27	.251	.666	0.0	1.0	1.801	2.0	.499	0.2	1.169	1.168	-0.09	1.168	-0.09	1.071	-8.38	1.126	-3.68
28	.752	.220	0.0	1.0	1.801	2.0	.504	0.8	1.714	1.724	0.58	1.724	0.58	1.676	-2.22	1.682	-1.87
29	0.0	.896	.250	.750	1.812	2.0	.590	18.0	1.052	1.120	6.46	1.120	6.46	1.004	-4.56	1.120	6.46
30	.242	.678	0.0	1.0	1.809	2.0	.520	4.0	1.142	1.162	1.75	1.162	1.75	1.069	-6.39	1.123	-1.66
31	.507	.493	0.0	.822	2.0	1.698	.503	0.6	1.236	1.239	0.24	1.239	0.24	1.018	-17.6	1.239	0.24
32	~.27	~.73	0.0	.825	2.0	1.702	>.59	--	--	--	--	--	--	--	--	--	--
33	.754	.254	0.0	.825	2.0	1.702	.510	2.0	1.424	1.454	2.11	1.454	2.11	1.213	-14.8	1.464	2.81
34	.285	.715	.30	.60	2.0	1.750	.517	3.4	1.484	1.528	2.96	1.542	3.91	1.388	-6.47	1.465	-1.28
35	0.0	1.0	.250	.618	2.0	1.702	>.648	--	--	--	--	--	--	--	--	--	--
36	.506	.407	0.0	1.0	1.701	2.0	.504	0.8	1.412	1.419	0.50	1.419	0.50	1.294	-8.36	1.331	-5.74
37	.254	.617	0.0	1.0	1.705	2.0	.501	0.2	1.124	1.125	0.09	1.125	0.09	0.980	-12.8	1.059	-5.78
38	.752	.204	0.0	1.0	1.702	2.0	.505	1.0	1.694	1.708	0.83	1.708	0.83	1.633	-3.60	1.642	-3.07
39	.285	.620	.30	.70	1.766	2.0	.514	2.8	1.481	1.517	2.43	1.547	4.46	1.400	-5.47	1.477	-0.27
40	0.0	.835	.25	.75	1.702	2.0	>.571	--	--	--	--	--	--	--	--	--	--
41	.504	.331	0.0	1.0	1.500	2.0	.504	0.8	1.330	1.339	0.68	1.339	0.68	1.118	-15.9	1.173	-11.8
42	~.26	~.74	0.5	0.0	2.0	1.0	>.535	--	--	--	--	--	--	--	--	--	--
43	1.0	0.0	.963	0.0	0.0	1.0	.502	0.4	2.691	2.962	10.1	3.852	43.1	3.709	37.8	3.709	37.8
44	.905	0.0	1.0	0.0	1.0	0.0	.513	2.6	2.622	2.715	3.54	3.620	38.1	3.276	24.9	3.276	24.9

Results for the (2/3,2,1) and (2,1/3,2) systems, which are the simplest and were included in the earlier Final Report, agree most often with theory. Note that for systems containing only one trifunctional ingredient, $r_f = r_s$.

Although the Flory model is most consistent with the data, observed percent deviations in r (Δr_f) are quite large in some cases. Since the largest deviations are for late gelling systems, the possibility of side reactions arises. But again we must ask: Why should side reactions occur only when monofunctional ingredients are present, since (3,2/3,2) systems obeyed the Flory model? A more logical conclusion is simply that none of the theories correctly accounts for monofunctional components.

D. Commercial Prepolymers

In this phase of the work the gel point method was applied to several carboxy- and hydroxy-terminated prepolymers to determine whether meaningful functionalities could be obtained.

1. Emery Diacid

The first of these was Emery Industry's Empol 1010 Dimer Acid, a carboxy-terminated prepolymer alleged to be completely difunctional with a molecular weight of 565. This product was used in place of sebacic acid in (2/3,2) systems containing PTA under excess hydroxyl conditions, in (2/3,2) systems containing TME and in (3,2/2) systems containing BTA under excess acid conditions, and in (3,2/3,2) systems containing PTA and TME under excess hydroxyl condition. The results are shown in Table 9; all mixtures contained 50% Nujol as solvent, except where noted. The average α-value for Runs 1-14 under excess alcohol conditions is $\alpha = 0.5002$, in excellent agreement with theory and with the further implication that the compound is indeed difunctional and its molecular

Table 9

GEL POINTS FOR SYSTEMS CONTAINING EMERY DIACID

Run	ρ_A	ρ_B	α	$\pm$	Excess
1	.205	0	.495	.019	OH
2	.245	0	.485	.005	OH
3	.303	0	.500	.008	OH
4	.403	0	.500	.005	OH
5	.510	0	.500	.005	OH
6*	.513	0	.500	.005	OH
7	.513	0	.502	.011	OH
8	.514	0	.504	.028	OH
9	.602	0	.500	.004	OH
10	.702	0	.501	.004	OH
11	.750	0	.513	.002	OH
12	.750	0	.502	.007	OH
13	.801	0	.501	.003	OH
14	.900	0	.500	.003	OH
15	0	.179	.706	.059	COOH
16	0	.433	>.559	--	COOH
17	0	.600	.634	.024	COOH
18†	.20	0	.705	.053	COOH
19†	.40	0	.613	.034	COOH
20	.037	.30	.577	.011	OH
21	.035	.50	.533	.014	OH
22	.042	.70	.540	.013	OH

* No solvent.
† Uses BTA.

weight is correct. Results from the (2/3,2) TME excess acid experiments (Runs 15-17) showed late gelation, as was observed for previous work with this crosslinker under excess acid conditions. The reasons for the late gelation in Runs 18-22 are as yet unknown.

2. Emery Triacid

The second prepolymer investigated was Emery's Empol 1040 Trimer Acid, a carboxy-terminated prepolymer alleged to be completely trifunctional with a molecular weight of 847, or 3/2 x mol. wt. of the Diacid. Gel point determinations were made for (2/3,2) systems with excess hydroxyls and (3,2/2) systems with excess acids using Trimer Acid, decanediol and sebacic acid.

Under these conditions, the functionality of the Trimer Acid may be calculated from the following theoretical considerations. Define:

B = meq OH contributed by the diol

A_3 = meq COOH contributed by the trifunctional component

A_2 = meq COOH contributed by the difunctional component

$A = A_2 + A_3$ = total meq of COOH present.

Then by substituting $r = B/A$ and $\rho = A_3/A$ in Eq. (1) we find

$$B = 2A_3 + A_2 \tag{4}$$

We now assume that the only species present in the Trimer Acid are the trifunctional species itself and a difunctional species whose molecular weight is 2/3 of that of the triacid (i.e., Dimer Acid). This assumption is not unreasonable in view of the manufacturer's description of the products.[12] We now let

T = meq of COOH contributed by the prepolymer

kT = meq of COOH on the trifunctional species

$(1-k)T$ = meq of COOH on the difunctional species

where $0 \leq k \leq 1$. Then Eq. (4) may be written

$$B = 2kT + A_2 + (1-k)T$$

or, rearranging,

$$k = \frac{B - A_2}{T} - 1 \tag{5}$$

For the excess carboxyl systems, $R = A/B$ and a similar treatment yields

$$k = \left(\frac{A_2 + T}{T}\right)\left(\frac{A_2 + T}{B} - 1\right) \tag{6}$$

The number-average functionality f_n is defined by

$$f_n = \frac{\sum_i a_i f_i}{\sum_i a_i} \tag{7}$$

where a_i is the mole fraction of species having f_i functional groups per molecule. For Trimer Acid this becomes

$$\frac{3k + 2(1-k)}{k + (1-k)} = 2 + k = f_n \tag{8}$$

The weighted average functionality of a polymer is defined as

$$f_w = \frac{\sum_i a_i f_i^2}{\sum_i a_i f_i} \; ;$$

if we assume that Trimer Acid is a mixture of tri- and difunctional species only, then

$$f_w = 5 - \frac{6}{f_n} \tag{9}$$

or

$$f_w = \frac{4 + 5k}{2 + k} \qquad (10)$$

Table 10 contains the results of experiments employing Trimer Acid as crosslinker. The data are plotted in Figure 1. The average k-value for the 11 excess hydroxyl runs is k = 0.930 (standard deviation = 0.040). This yields f_n = 2.930 and f_w = 2.951. For the nine excess acid runs, average k = 0.788 (standard deviation = 0.259) or f_n = 2.788, f_w = 2.848. The reason for the discrepancy in k is unknown; however, such behavior is not totally unexpected in view of the results for model compounds.

3. Hystrenes

Several Hystrene carboxy-terminated prepolymers were obtained from Humko. Each sample is a blend of a trifunctional, a difunctional and, in some cases, a monofunctional carboxy-terminated prepolymer. Efforts on our part to obtain the structures of these products from the manufacturer were unsuccessful. The composition of the various Hystrenes, as supplied by the manufacturer, are shown in Table 11.

Table 11

COMPOSITION OF HYSTRENES

Sample	Trimer (%)	Dimer (%)	Monomer (%)
3695	4	95	1
3680	17	83	Trace
3675	25	75	Trace
5480	80	20	Trace

Molecular weight of the dimer is 570 and of the trimer 855 (=3/2 x 570). The results of gel point determinations made for systems using the Hystrenes are shown in Table 12. Additional ingredients were sebacic

Table 10

GEL POINTS FOR SYSTEMS CONTAINING EMERY TRIACID

Run	ρ_A	R	α	$\pm$	k	Excess
1	.098	1.097	.449	.016	1.0069	OH
2	.198	1.196	.500	.012	1.0020	OH
3	.285	1.253	.530	.013	.8883	OH
4	.379	1.345	.522	.008	.9176	OH
5	.481	1.442	.521	.021	.9203	OH
6	.576	1.546	.512	.008	.9474	OH
7	.651	1.609	.517	.007	.9358	OH
8	.727	1.663	.520	.010	.9247	OH
9	.813	1.735	.524	.007	.9036	OH
10	.871	1.786	.523	.012	.9018	OH
11	.937	1.827	.531	.006	.8829	OH
12	.10	1.067	.599	.019	.6699	COOH
13	.20	1.147	.577	.011	.7346	COOH
14	.30	1.227	.570	.008	.7557	COOH
15	.40	1.306	.567	.011	.7648	COOH
16	.50	1.409	.550	.010	.8182	COOH
17	.60	1.492	.550	.010	.8190	COOH
18	.70	1.572	.551	.017	.8165	COOH
19	.80	1.687	.538	.010	.8588	COOH
20	.90	1.758	.539	.011	.8538	COOH

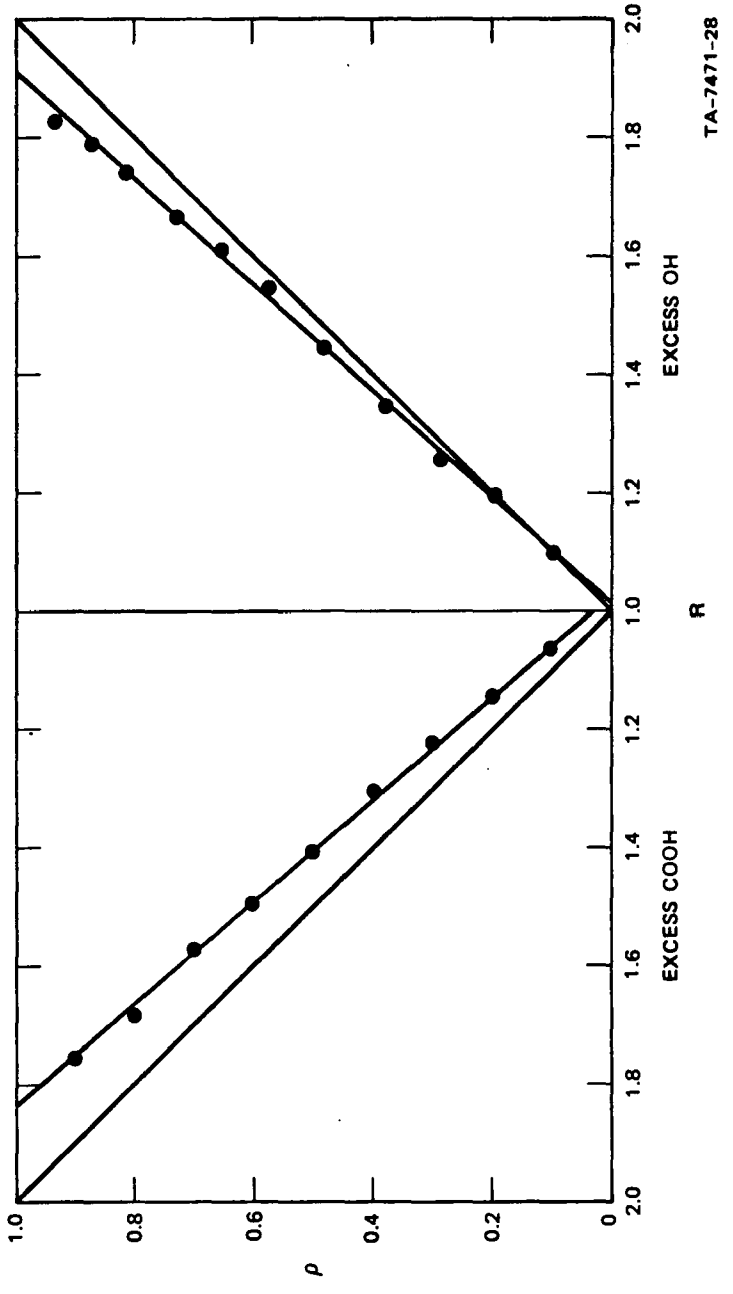


FIGURE 1 GEL POINTS FOR SYSTEMS CONTAINING TRIMER ACID

Table 12

GEL POINTS FOR HYSTRENE SYSTEMS

Run	Sample	ν^*	Excess	R	±	R_{theo}	$\Delta R^\dagger$
1	3675	1.0	COOH	1.100	0.012	1.250	0.150
2	3675	0.97	OH	1.216	0.040	1.242	0.026
3	3680	1.0	COOH	1.009	0.012	1.170	0.161
4	3680	0.92	OH	1.110	0.012	1.156	0.046
5	3695	0.75	OH	1.178	0.023	1.271	0.093
6	3695	0.78	OH	1.170	0.006	1.273	0.103
7	5480	0.93	OH	1.690	0.035	1.744	0.050

* mole fraction of prepolymer in the mixture.

† $R_{theo}-R$.

acid, decanediol and, in some cases, PTA; Nujol was used as solvent (50% by weight) in all cases. R_{theo} is calculated from Stockmayer's equation

$$R_{theo} = 2\rho_A + \sigma_A$$

where values for ρ_A and σ_A are based on the compositions given in Table 11.

In general, the largest ΔR's are for excess carboxyl conditions, as has been observed for most other systems. This may be due to unequal reactivity of the carboxyl groups in the trifunctional species. All of the systems gelled late ($R < R_{theo}$) which may be explained several different ways, the most probable of which is incorrect composition data from the manufacturer. Lack of time prevented a more complete study of these prepolymers.

4. Telegen-S

Preliminary data were obtained for General Tire's Telegen-S, a difunctional, saturated, primary hydroxy-terminated polybutadiene. First, the molecular weight of this compound was determined by vapor phase osmometry. Based on a value of 2290 and assuming complete difunctionality, several runs were made on (2/3,2) systems containing sebacic acid and PTA under excess hydroxyl conditions and with 0-50% Nujol as solvent. On observing early gelation in all cases (yielding meaningless data since gelation occurred at the first composition tried), one experiment was conducted where PTA was added in small increments to a 50/50 mixture of Telegen-S and Nujol. The system became dark after $\sim$ 12 hr and gelled very slowly at $\alpha = 0.379 \pm 0.042$. The reason for the large deviation from $\alpha = 1/2$ is not known; oxidative crosslinking should not be occurring since the manufacturer reports only 0.9 mm/g maximum unsaturation in the product. Once again, lack of time prevented a more thorough investigation of this and related prepolymers.

REFERENCES

1. a) Marsh, H. E. and Hutchison, J. J., JPL Space Programs Summary 37-48, Vol. II, 95 (1967).

   b) Marsh, H. E., Jr. and Hutchison, J. J., Chemical Propulsion Information Agency Pub. No. 187 (CONFIDENTIAL), 55 (1969).

2. Flory, P. J., J. Amer. Chem. Soc. 63, 3083 (1941).
3. Hodgkin, J. H., Martinelli, F. J., and Heller, J., Final Report, Contract NAS 7-689, Oct. 1970.
4. Stockmayer, W. H., J. Chem. Phys. 11, 45 (1943).
5. Stockmayer, W. H., J. Polym. Sci. 9, 69 (1952).
6. Marsh, H. E., unpublished results.
7. Newman, M. S. and Lowrie, H. S., J. Amer. Chem. Soc. 76, 6196 (1954).
8. Flory, P. J., J. Amer. Chem. Soc. 63, 3091 (1941).
9. Flory, P. J., J. Amer. Chem. Soc. 63, 3096 (1941).
10. Stockmayer, W. H., private communication.
11. H. E. Marsh, J. Heller, J. H. Hodgkin, and F. J. Martinelli, Polymer Preprints 12, 598 (1971).
12. A. W. Fogiel and C. W. Stewart, J. Polymer. Sci. 7, 1116 (1969).
13. Technical Bulletin 438A, Empol 1040 Trimer Acid, Emery Industries.

Appendix

METHOD OF EXTRAPOLATION OF TYPE-Y DATA

The incipient gel point of a polymer mixture is that point below which the mixture's viscosity is finite and above which it is infinite. For Type-Z systems,* this point is easily obtainable since there is an abrupt change in viscosity, from a measurable (and usually rather low) value to a very high unmeasurable value. Type-Y systems,* however, do not behave this nicely; instead, the viscosity-versus-R curves resemble the curve shown in Figure 5 of the Final Report, 1968-1970, with no distinct gel point. Clearly these curves are tending to infinity, and the problem is then to determine the exact point at which the viscosity becomes infinite. One way to approach this problem is to find a function that will approximate these curves and that has a point in its domain where it becomes indefinitely large.

Thus, we seek a function f such that

$$\eta = f(R) \qquad R > R_c$$

and

$$\lim_{R \to R_c} f(R) = \infty$$

A general function satisfying these criteria is

$$f(R) = \sum_{n=1}^{\infty} \frac{a_n}{(R-R_c)^n} \tag{A-1}$$

---

* See the Final Report, 1968-1970, Part B for discussion of Type-Y and Type-Z systems.

where the a_n are positive constants. The sufficient condition for this series to converge (absolutely) is that

$$\frac{a_{n+1}}{a_n} < R-R_c \tag{A-2}$$

From condition (A-2) we find the recursion formula

$$a_{n+1} = K_n a_n (R-R_c)$$

where K_n are constants and $K_n < 1$ for all n. Then we have

$$\begin{aligned} a_2 &= K_1 a_1 (R-R_c) \\ a_3 &= K_1 K_2 a_1 (R-R_c)^2 \\ &\vdots \\ a_{n+1} &= \left(\prod_{i=1}^{n} K_i \right) a_1 (R-R_c)^n \\ &\vdots \end{aligned} \tag{A-3}$$

Note that since $(R-R_c)$ can always be kept less than 1, $a_{n+1} \to 0$ as $n \to \infty$. Substituting the expressions (A-3) into Eq. (A-1) yields

$$f(R) = \frac{a_1}{R-R_c} \left[1 + \sum_{n=1}^{\infty} \prod_{i=1}^{n} K_i \right] . \tag{A-4}$$

We further require that

$$\prod_{i=1}^{n} K_i < b_n$$

for sufficiently large n, where the b_n are constants and

$$\sum_{n=1}^{\infty} b_n < \infty \quad .$$

Then the series in Eq. (A-4) converges; denote the value of this series by K, then

$$f(R) = \frac{a_1 (1+K)}{R-R_c} \qquad \text{(A-5)}$$

If we now define a new function

$$g(R) = \frac{2}{R-R_c}$$

then f = Ag, where A is a constant, and

$$\lim_{R \to R_c} f(R) = \lim_{R \to R_c} g(R) = \infty \quad .$$

Consider the set of experimental data (R_i, η_i), i=1,2,...,N where N is the number of points for a given value of ρ and $\eta_i = f(R_i)$ for each pair. Now let

$$\eta_i^* = g(R_i) = \frac{2}{R_i - R_c}$$

for all i. With the aid of a computer, values of η_i^* were calculated from known R_i values for different values of R_c. Eact set of η_i^*s so calculated was substituted in the equation

$$\eta^* = a\eta + b \qquad \text{(A-6)}$$

where the constants a and b were calculated by the method of least-squares. The coefficient of correlation for this equation was calculated for each value of R_c according to

$$C = \left[\frac{\sum_{i=1}^{n} [(a\eta_i + b) - \bar{\eta}]^2}{\sum_{i=1}^{n} (\eta_i - \bar{\eta})^2} \right]^{1/2}$$

where

$$\bar{\eta} = \frac{\sum_{i=1}^{N} \eta_i}{N}$$

The value of R_c that yielded the largest value of C was taken as the answer.